Methodology for Chemical Characterization of Exhaust Emissions from Heavy Duty Trucks and Buses fueled by Diesel and CNG

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ABSTRACT

A collaborative technology validation program was conducted for over a year (Fall 1999 - Spring 2001) to evaluate ultra-low sulfur diesel (ULSD) fuels and passive diesel particle filters (DPF) in several heavy-duty vehicle fleets in Southern California. Detailed description of the study design and results obtained to-date can be obtained at the study website: http://www.ecdiesel.com. In the second round of testing, a few of the vehicles were selected for chemical characterization of volatile, semi-volatile, and particle bound compounds. During the second round of testing, two transit buses, fueled by CNG, were added to the test matrix in addition to the diesel ones.

This paper focuses on presenting the sampling and analysis methodology used for characterizing the exhaust emissions. It describes the lessons learned and highlights methodology issues. A small sample of the results is used to highlight issues of tunnel blanks and variability issues when characterizing exhaust emissions at very low concentrations.

INTRODUCTION

New ultra-low sulfur diesel formulations, known as ECD and ECD-1, were developed by ARCO, a BP company. These fuels enable the retrofit and operation of diesel particle filters (DPF) that dramatically reduce diesel PM, total hydrocarbons (THC), and carbon monoxide (CO) emissions. An industry-government collaborative study was launched as a demonstration program to evaluate these new diesel formulations and catalyzed particle filters in on-road fleets

This collaborative multi-year program consisted of two rounds of vehicle tests to characterize regulated and unregulated exhaust emissions. The overall test program consisted of seven vehicle fleets and more than 150 vehicles. Field-testing was performed via a transportable chassis dynamometer based laboratory designed and operated by West Virginia University (WVU).

The second and final round of testing conducted during March – May 2001 was designed to evaluate both the durability of the control devices, after a year of on-road operation, and to characterize the chemical species in the vehicle exhaust. For this purpose a subset of vehicles was selected – a school bus, two grocery-truck tractors, and three transit buses. The vehicles
were tested with the original exhaust system and subsequently fitted with DPFs provided by Engelhard (DPX™) and Johnson-Matthey (CRT™). A team from Desert Research Institute (DRI) conducted the on-site analysis of VOCs by GC-MS, while the other analyses were performed at the DRI laboratories in Reno, NV. Alta Analytical Laboratory of El Dorado Hills, CA, analyzed selected samples for dioxins and furans.

Detailed results from these tests were previously reported\(^3\) and have shown that vehicles retrofitted with DPFs and fueled with ULSD emitted, on a per mile basis, 80% to 98% less PM, CO and organic compounds when compared to CARB diesel fueled vehicles with their original exhaust systems. This paper aims to highlight the sampling and analysis methods used and share the lessons learned together with some key results.

**METHODOLOGY**

The goal of the chemical characterization phase of the study was to determine relative changes in the emissions of key compound classes under different operational scenarios. Vehicle emissions resulting from operation on CARB diesel fuel were taken as the normative baseline, and each of the vehicles was profiled by comparing its CARB diesel performance to that of several fuels and after-treatment technology combinations.

**Test Fuels**

The test fuels used included: market average CARB diesel, BP’s emissions control diesels (ECD and ECD-1), a synthetic diesel (Fischer-Tropsch, or F-T), and compressed natural gas (CNG). Both ECD and ECD-1 are produced from typical crude oil using a conventional refining process, and have low sulfur content. They differ in their aromatic compounds content and their Cetane number. Both ECD and ECD-1 have less than 15 ppm sulfur. ECD-1 is currently available commercially throughout California.

The F-T diesel used was produced by Shell's synthesis plant (Bintulu, Malaysia). This F-T diesel was previously used by the US DOE National Renewable Energy Laboratory (NREL) in studies described elsewhere\(^4\). The CNG used for testing is commercial grade CNG composed of at least 88-mol% Methane in a blend with other higher hydrocarbons, meeting or exceeding California specifications. It also contains residual amounts of sulfur compounds.

**Vehicle Testing**

The heavy heavy-duty vehicles tested were fueled with CARB diesel and the new ULSDs (ECD and ECD-1) and with one of two after-treatment devices. In addition, the school bus was also tested with F-T diesel with and without a diesel particle filters (DPX™). One of the grocery trucks tested was fueled with both CARB diesel and ECD-1 and tested with and without CRT™, while the second grocery truck was tested only with ECD-1 and DPX™. The transit buses were all of similar type and build yet designed to operate on different fuels, either diesel or CNG. The diesel fueled transit bus was also outfitted with a CRT™ without a separate oxidation catalyst.
The driving cycles used were the City Suburban Heavy Vehicle Route (CSHVR) for the school bus and the grocery trucks and the Central Business District (CBD) cycle for the transit buses. All tests were repeated three times, and vehicles equipped with after-treatment devices were sampled using double-length cycles (back-to-back) with a single set of filter media, to ensure collection of sufficient sample for analysis.

WVU’s Transportable Laboratory includes a chassis dynamometer laboratory and a vehicle exhaust dilution tunnel. Vehicle exhaust was diluted in the total exhaust double-dilution CVS, and both regulated and unregulated emissions were determined. The total exhaust dilution tunnel was designed and built in accordance with the requirements of the U.S. EPA Regulations. The tunnel simulates ambient conditions and allows measurements of exhaust constituents in both gaseous and particle form. The primary dilution tunnel was supplied with dilution air with the capability of providing up to 3,000 scfm of HEPA filtered air (99% removal efficiency) to the dilution tunnel. The high removal efficiency of the HEPA filter eliminated random errors that could interfere with measurements of low levels of PM when ambient PM levels are variable.

**Sampling System**

Figure 1 Depicts schematically the sampling system used for chemical characterization.

![Vehicle Exhaust Sampling System](image)

**Figure 1. Vehicle Exhaust Sampling System**

<table>
<thead>
<tr>
<th>ID</th>
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<tr>
<td>1</td>
<td>HC</td>
<td>9</td>
<td>Carboxyls</td>
</tr>
<tr>
<td>2</td>
<td>CO/CO2</td>
<td>10</td>
<td>PM2.5 (mass &amp; metals)</td>
</tr>
<tr>
<td>3</td>
<td>NOx</td>
<td>11</td>
<td>PM2.5 (EC/OC &amp; Ions)</td>
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<tr>
<td>4</td>
<td>TEOM</td>
<td>12</td>
<td>PM10 (mass &amp; SOF)</td>
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<tr>
<td>5</td>
<td>TPM</td>
<td>13</td>
<td>Particulate PCDD/PCDF</td>
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<tr>
<td>6</td>
<td>Particulate PAHs</td>
<td>14</td>
<td>Volatile PCDD/PCDF</td>
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<tr>
<td>7</td>
<td>Semi-Volatiles Organics</td>
<td>15</td>
<td>Bioassays</td>
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<tr>
<td>8</td>
<td>Gaseous VOCs</td>
<td>16</td>
<td>Bioassays</td>
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The ports numbered 1-5 were used for regulated emissions. All measurements were done in accordance with the procedures in 40CFR, Part 86; Subpart N, as appropriate. Ports numbered 6-16 were added for this study to collect exhaust samples for chemical characterization. The features incorporated into the total exhaust primary dilution tunnel include:

- A secondary dilution tunnel for Total PM (TPM) sample collection for gravimetric analysis.
- A “Speciation Cart” for the collection of diluted diesel exhaust samples at flow rates up to five scfm (142 lpm), allowing proportional sampling matching transient operation of vehicle.
- Heated sample lines controlling the temperature of the sample stream coming into the “Cart”, for sampling of volatile, semi-volatile and carbonyl compounds.
- PM\textsubscript{2.5} and PM\textsubscript{10} cyclones for collection of size segregated particulate matter samples.

Quality Assurance/Quality Control

Specific steps were incorporated into the study design, which included among others:

- All the sampling media were prepared and pre-cleaned at DRI laboratories prior to being shipped to the field.
- All gravimetric determinations conducted in the field were repeated in the laboratory after re-conditioning of the exposed filters.
- A complete set of tunnel background samples (for all analytes) was collected along with a set of field blanks that traveled from the laboratory to the field and back.
- Ambient measurements of VOCs were conducted in conjunction with sample collection, since the tunnel inlet air was not scrubbed for hydrocarbons.
- Full chain-of-custody procedures were used to track sample and data movement.

Background Samples

In anticipation of low sample concentration and mass collected during vehicle testing, extensive amounts of background data were collected and analyzed to differentiate between ambient background, tunnel contribution and engine-out emissions. Three types of background samples were normally collected: ambient, pre-test tunnel, and post-test tunnel background.

Post-HEPA filter ambient background samples for VOC were collected for 3 to 6 hours at the beginning of each test day. Pre-test background samples were collected from the dilution tunnel. The pre-test procedure consisted of operating the primary dilution tunnel with the vehicle’s engine turned off and sampling the ambient air in the tunnel for a duration equivalent to the time for that day’s test run. At the end of the test day, a post-test background was collected similarly.

Sample Collection and Analysis

A detailed sampling and analysis plan was developed specifying all sample collection and analysis procedures. The plan listed target compounds for identification and quantification along with minimum detection levels expected.

A detailed listing of all collection devices and analysis employed is given in Table 1.
In the section below we will present a brief discussion of some of the methods used for vehicle emissions characterization:

- Gravimetric analysis of PM$_{10}$, PM$_{2.5}$, and TPM
- Inorganic species (including ions, elements and OC/EC)
- Gas phase volatile organic compounds (VOC)
- Carbonyl compounds
- Particle-bound and semi-volatile organic compounds (PAHs, n-PAHs, PCDD and PCDF)
**Particulate Matter**

All particulate matter masses were determined by gravimetric analysis. The TPM results correspond to the total particulate mass captured on Teflon coated glass-fiber filters, following the Federal Test Procedure. PM$_{2.5}$ and PM$_{10}$ samples were collected on Teflon and Teflon coated glass-fiber filters, respectively, preceded by size selective cyclones, as described above. The integrated masses of emissions for each constituent were calculated by employing the equations from 40 CFR Part 86 Subpart N.

**Inorganic Species**

Methodology for the collection and analysis of particle mass by gravimetry, carbon by thermal/optical reflectance (TOR), ions (sulfate, nitrate) by ion chromatography, and elements by x-ray fluorescence have all been described elsewhere.

Briefly, Teflon filters were weighed prior to and after sampling in a temperature - and humidity-controlled environment (20°C, 30% RH) to determine mass concentrations. After being weighed, these filters were analyzed for trace elements by x-ray fluorescence. A 0.56 cm$^2$ punch from the pre-fired, quartz-fiber filters was analyzed for “organic” and “elemental” carbon (OC/EC) by the thermal optical reflectance (TOR) method. Half of the quartz filter was extracted in 10 ml of deionized water, and the extract was analyzed for nitrate, sulfate, and chloride ions by ion chromatography.

**Volatile Organic Compounds (VOC)**

VOC samples were collected using Tedlar bags and were analyzed on-site within 2-hrs of sample collection by a GC/MS method. A portable system consisting of a Gas Chromatograph/Mass Spectrometer and a Flame Ionization Detector (GC/MS/FID) equipped with a cryogenic pre-concentrator was used in the field for these measurements, following a modified EPA method TO-15 technique. Further details of the method are provided in Appendix A.

This on-site GC/MS/FID system was viewed as essential to allow for analysis of the collected Tedlar bags within a very short time window and prevent – or at least minimize - degradation of the samples. Although samples were analyzed within 2 hours of collection, the possibility existed that significant losses of 1,3-butadiene occurred after sampling. In this study gaseous samples were collected in Tedlar bags that were pre-cleaned differently from the way CARB normally pre-cleans their Tedlar bags. The main difference is that CARB uses a heat treatment to remove contaminants during the pre-cleaning process. However, it is unknown if this has affected the stability of the 1,3-butadiene samples.

**Carbonyl Compounds**

The measurement technique used for carbonyl compounds is an established procedure (EPA Method TO-11A) using 2,4-dinitrophenylhydrazine (DNPH) impregnated Si Sep-Pak cartridges (Waters Associates, Milford, MA). Carbonyl compounds collected in the cartridges (as hydrazones) were eluted with 2 ml of HPLC grade acetonitrile and analyzed by HPLC (Waters 2690 Alliance System with 996 Photodiode Array Detector) as previously described. A 3.9 x 150 mm C18 column (Nova-Pak, Waters, Inc.) with gradient elution (solvent A: water, solvent B: acetonitrile) was employed.
A series of two Sep-Pak cartridges were used for the collection of Carbonyl compounds from the exhaust and each sample was analyzed individually to allow for determination of breakthrough.

**Polycyclic Aromatic Hydrocarbons (PAHs and nitro-PAHs)**

All sampling media were extracted and pre-cleaned prior to shipment to the field for sample collection. The sampling cartridges used included two 2” round PUF plugs with 10 g XAD resin in between. The PUF cartridges were cleaned by rinsing with distilled water, followed by Soxhlet extractions with 10% diethyl ether in hexane, followed by acetone. The XAD resin was cleaned with methanol followed by dichloromethane (DCM) Soxhlet extraction for 24 hr. The 70mm TIGF (TX40HI20-WW) filters were cleaned by Soxhlet extraction with methanol, followed by DCM.

For each sample collected, the PUF/XAD/PUF cartridges and the filters were extracted and analyzed separately. Prior to extraction, the PAH and n-PAH deuterated internal standards were added to each filter and cartridge pair. Authentic PAH and nitro-PAH standards (purchased from Aldrich, Inc., and Accustandard) plus National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1647 (certified PAH), were used to make calibration solutions. A three-level calibration was performed for each compound of interest and the calibration check (using median calibration standards) were run every ten samples to determine accuracy. If the relative accuracy difference from the standard value was greater than 20%, the instrument was recalibrated. Further details on the extraction and analysis procedure are provided in Appendix A.

**Polychlorodibenze Dioxins and Furans (PCDD/PCDF)**

Appropriate samples for this analysis were collected to screen for PCDD/PCDFs, but only ten pre-selected samples were analyzed for dioxins and furans. If positive hits were found, the remainder of the samples would then be available for further analysis. All samples were handled per EPA method TO-9. First, each separate cartridge was spiked with $^{13}$C labeled dioxins prior to shipment to the field. These spiked compounds were used to determine the recovery as part of the calculation for the target compounds. The target compounds included dioxins and furans with varying degrees of chlorination; detection limits below 10 pg/sample were achieved for the tetra-chloro, below 50 pg/sample for penta- through hepta- and below 100 pg/sample for octa-chloro compounds.

**RESULTS AND DISCUSSION**

All analytical data obtained by the laboratories was sent to both NREL and WVU. All the results were normalized to reflect the composite test mileage for proper comparison of the fuel and after-treatment effects in terms of (mass emitted)/(miles traveled). WVU reduced the data to account for the volume sampled in a given run and the mileage ‘driven’. Appendix B provides further details on the data reduction method. All data were then transmitted to NREL for final quality control and archiving.

No data included in the archive has been corrected for background levels, due the inability to assign a specific background level to a specific sampling event. As a consequence, the data for both ambient and tunnel backgrounds are documented alongside the measurement data in the
final master database. A small subset of the results obtained is provided below along with discussion of main observations.

**Particulate Matter**

The tunnel background data demonstrate that the HEPA filter installation on the inlet air to the dilution tunnel has resulted in background levels that are one or two orders of magnitude lower than the vehicle emissions. This reduction in background enables better characterization of the comparative emission profiles with and without the DPFs, respectively, as exemplified by the results in Figure 2, which summarizes the results for the diesel and CNG transit buses. The buses were chosen to have similar engines and chassis configurations, with the only variable being the operating fuel. For the diesel fueled transit bus, the TPM and PM\(_{10}\) emissions are quite similar (within 10%), while the PM\(_{2.5}\) are lower, for all the diesel fuels tested. In evaluating the PM\(_{10}\) and PM\(_{2.5}\) results for the ULSD without a DPF it is evident that these emissions are lower than those measured for the buses fueled by CARB diesel fuel. Specifically, the emissions exhibit about a 40% reduction for the ECD-1 fuel compared to the CARB diesel fuel.

![Figure 2. Particulate Matter Levels for Diesel and CNG Fueled Transit Buses](image)

**Inorganic Species**

Data summaries for the inorganic species and Elemental/Organic Carbon (EC/OC) follows the procedure outlined for particulate matter above. All the data were previously reported, and will not be repeated here\(^8\). EC/OC, elements and ions were measured for PM\(_{2.5}\) samples only. It was observed that for the vehicles running on all fuels without the trap, OC constitutes 34 – 36% of total carbon (TC), whereas for the same vehicles running with the trap, OC accounts for 92 -
93% of TC. The tunnel background samples are composed essentially of OC only (98 – 99% OC). For the tunnel background samples, the OC fractions seem to be composed mainly of gaseous organic compounds that are adsorbed on the quartz filters during sample collection (positive filter artifact). Teflon membrane filters that have been used for gravimetric analyze, have much smaller exposed surface area and are thus less prone to organic gases adsorption. In contrast, the DPF equipped vehicles exhibit a lower contribution of TC to the fine particle mass. For these vehicles the fine particle mass is an order of magnitude lower and seems to be primarily composed of SO₄²⁻, NO₃ and NH₄⁺ ions and the elements Ca, Mg and Zn.

Volatile Organic Compounds (VOCs)

In order to make the data analysis for VOCs more manageable, the 95 identified compounds were grouped into one of five compound classes:
- C₂ – C₅ Alkanes: light saturated hydrocarbons
- C₆ and higher Alkanes: all remaining saturated hydrocarbons
- C₂ – C₅ Olefins: light olefin compounds with one or more unsaturated bonds
- C₆ and higher Olefins: all remaining olefin compounds
- Aromatics: all aromatic compounds (up to C10) with at least one benzene ring

Figures 3 provide a summary of total VOCs segregated into the five compound groupings discussed above for the transit buses testing.

![Figure 3. Grouped VOC Emissions for Diesel and CNG Fueled Buses](image-url)
In reviewing the data for the transit buses, it is clear that those fueled by CNG have VOC emissions that are over an order of magnitude higher than the diesel fueled buses, showing significant levels of low molecular weight olefin and alkane emissions. The data is presented with a graph-within-a-graph in order to allow better articulation of the fuel and control technology effects. It is important to note that both the diesel and the CNG fueled vehicles were equipped with their original muffler without an oxidation catalyst. For the diesel buses tested with a DPF, the original muffler was replaced by the tested DPF.

Careful examinations of the data for each species reveals that for some compounds, most notably 1,3-butadiene, the trace levels detected in ambient air, tunnel backgrounds, and exhaust samples are very near the analytical detection limit. One can also hypothesize that absorption and desorption from the tunnel walls is likely to cause variability in the measurements, especially under the low concentration conditions observed here. These factors make it difficult to discern trends from the emissions data, for some of the compounds. In addition to tunnel effects, we might also be observing a degradation of some reactive VOCs, such as 1,3-butadiene due to its instability in the exhaust matrix.

The results demonstrate that in most cases diesel particle filters reduce total hydrocarbons, as measured by the total VOCs by over 70%. When comparing these GC/MS measurements with those obtained from continuous total hydrocarbon analyzers (THC) we find that the THC is consistently higher. The GC/MS method identifies the individual hydrocarbons peaks and sums them to generate the total in the exhaust (through C_{12}), while the THC analyzer uses an FID sensor calibrated with a single hydrocarbon. This might lead to the bias between the two methods although the total hydrocarbon analyzer used for continuous measurements meet all CFR requirements.

**Carbonyl Compounds**

The data from each of the sampling cartridges was evaluated for potential breakthroughs from the front to the back. Relatively high levels of ketones, such as acetone and MEK, were found on the 2nd cartridge (up to 50% of the first cartridge), which might be due to the breakthrough from the first cartridge. It has been observed, that acetone and MEK have higher tendency to breakthrough than aldehydes, especially in higher relative humidity (K.Fung, personal communication). The aldehyde data presented here does not include any appreciable breakthrough (determined for this study as the amount of aldehyde on the 2nd-cartridge > 30% of the amount of aldehyde on the 1st-cartridge) with the exception of the results for CNG Buses.

Results from the analysis of the individual cartridges were summed up and converted to a mass emission factor per unit of distance, as represented by the dynamometer tests. Data are presented in terms of “test, non-corrected” and “tunnel background” separately. Each of these values is presented along with its corresponding measurement uncertainty that takes into account replicate precisions, detection limits and the variability of the field blanks. This uncertainty provides some indirect measure for the potential for passive absorption of ambient carbonyls on the sampling cartridges when transported to and from the laboratory. cartridges when transported to and from the laboratory.
Figures 4 and 5 provide graphical representation of Carbonyl emissions for the school bus and the transit buses, respectively. Data shown here for formaldehyde and acetaldehyde only.

**Figure 4. Carbonyl Compounds Emissions from School Bus**

**Figure 5. Carbonyl Compounds Emissions from Transit Buses**
The fuel and after-treatment profiles for both compounds are similar, for all diesel fuels, with acetaldehyde < than 50% of the mass per mile for formaldehyde. For the transit buses fueled by CNG, the emissions of both formaldehyde and acetaldehyde are an order of magnitude higher than for any of the diesel fuels. In all cases where a DPF was installed, the emission levels have been reduced by over 95%.

**Polycyclic Aromatic Hydrocarbons (PAH and n-PAH)**

The determination of PAHs and n-PAHs entailed separate extraction and analysis of the filters and the cartridges, however in summarizing the results, the sum of the two is used since their apportionment between the vapor and particle phase is variable and highly dependent on exhaust temperature and sampling tunnel conditions. Therefore, providing data separately for the particle-PAHs vs. the vapor-PAHs is not meaningful and does not represent the true phase distribution of the compounds in the exhaust air when it is diluted into the ambient atmosphere.

For ease of data analysis and presentation, sums of total PAHs and nitro-PAHs were generated, as reported before. They were derived by subdividing the PAH compounds into groups based on the number of aromatic rings in their polycyclic skeleton, namely 2-rings, 3-rings, 4+ rings PAH compounds. For compounds of identical molecular composition, all the isomeric structures are lumped together since the analytical methods are not always capable of distinguishing them.

Figures 6 and 7 depict – as an example - the results for the emission of 3-ring PAH compounds for the school bus and the transit buses, respectively.

![Figure 6. Emissions of 3-rings PAH compounds from School Bus](image)
For the school bus both ECD and ECD-1 shows a higher emission level than F-T diesel, which contains no aromatic constituents. When equipped with a DPF all fuels exhibit the same emissions level.

For the transit buses, the diesel fueled bus with ECD+CRT shows a slightly higher level of emissions, while the bus with ECD-1+CRT shows a lower level of emissions than those observed for the CNG fueled buses. It is not clear that this is a fuel effect, since ECD has a lower aromatic content than ECD-1 (10% and 20%, respectively).

![Figure 7. Emissions of 3-rings PAH compounds from Transit Buses](image)

The overall results obtained for the PAHs, clearly show a higher abundance of the 2-ring compounds, as expected. Two ring PAHs are often the result of unburned aromatic compounds in the fuel. However, the data demonstrate that the DPFs are very effective in removing over 90% of the 2-ring PAH compounds from the exhaust emissions of diesel vehicles equipped with either a CRT™ or a DPX™, and have equal or lower emissions than for the CNG fueled transit buses.

In this study, we have also quantified a range of nitro-substituted PAHs. These compounds are known to be formed in the ambient atmosphere, however both the exhaust and the tunnel conditions, may promote their formation due to the presence of a radical rich combustion by-products mixture. The sampling tunnel provides a longer residence time than the exhaust manifold and could result more readily in quantifiable amounts of n-PAHs in the collected samples. In testing for n-PAHs, the low levels obtained and the need for repeated cleaning of the collected samples made it difficult to ascertain the origin of the observed compounds.
SUMMARY

This study has enabled us to demonstrate the general trends of the emission profiles for key compound classes when using the various fuels and control technology combinations for a range of heavy-duty vehicles. In general it is clear that emissions vary insignificantly merely by switching diesel fuel formulations. The biggest changes are affected by the introduction of ULSD and DPFs, and in these cases the emissions were the same or lower than those observed with CNG fueled buses.

The key learning and observations from this study are:

- Emissions reductions attributable to DPFs are in the range of 70-98%, when accounting for variability associated with individual vehicles and test days.
- Total VOC emissions are reduced by 70% for diesel-fueled vehicles equipped with DPFs.
- Aldehyde emissions are reduced by over 95% for ULSD fueled vehicles equipped with DPFs as compared to the CARB diesel baseline.
- THC emissions, measured by continuous analyzers with an FID, are typically greater than the sum of individually identified VOCs determined by GC/MS.
- Total VOC, acetaldehyde and formaldehyde emissions for CNG fueled transit buses are approximately an order of magnitude greater than the emissions from a comparable diesel fueled transit bus, both for conventional or ultra-low sulfur diesel fuel.
- Acetaldehyde emissions are approximately 50% of the formaldehyde emissions for diesel-fueled vehicles without after-treatment.
- The results for 2, 3, and 4+ ring PAHs compounds demonstrate that DPF equipped heavy-duty vehicles emit lower – or similar - levels of these compounds as compared to CNG fueled vehicles.
- Emissions of nitro-PAH are very close to the methods’ detection limits, and further investigation of the roots of these emissions might be warranted if more sensitive quantification methods are available.
- No dioxins or furans were observed in the vehicle exhaust collected in this study.
- Levels of 1,3-butadiene were observed to increase overnight, between the evening tunnel background and morning tunnel background runs. No explanation is offered for this trend. However, improved sampling and analysis techniques are needed for future studies to optimize the measurement of 1,3-butadiene.
- Great care needs to be taken in designing and executing such sampling and analysis test programs, especially when expected concentration are near, or at, background levels.

ACKNOWLEDGEMENTS

We would like to acknowledge the great collaboration by all participants. In particular, we wish to recognize the fleets that that provided their vehicles for the extended testing required for this study: San Diego Unified School System, Los Angeles Metro Transit Authority, and Ralph’s Grocery Stores.
REFERENCES


KEY WORDS

Low sulfur diesel; Heavy-Duty Vehicle Emissions; Vehicle Exhaust; Dilution Tunnel; Volatile Organic Compounds; Carbonyl Compounds; and Polycyclic Aromatic Compounds.
APPENDIX A: Analysis Methods

Volatile Organic Compounds
On-site VOC analysis was conducted using a GC/MS/FID system. The GC/MS system included: an Entech 7100 pre-concentrator, a Varian 3800 gas chromatograph with FID and column switching valve, and a Varian Saturn 2000 ion trap mass spectrometer. The Entech preconcentrator consisted of three traps: 50% glass beads/50% Tenax, held at −100 °C during sample transfer, 100% Tenax held at −40 °C and a final focusing trap (a piece of silico-steel capillary) held at −180 °C. The sample is desorbed from the first trap at 10 °C, from the second trap at 200 °C and from the third one at approximately 70 °C to a transfer line heated to 110 °C and connected to the head of the first column.

The sample was injected at the head of a 60 m x 0.32 mm polymethylsiloxane column (CPSil-5, Varian, Inc.) held at 30 °C. This column was connected to the switching valve leading into a 30 m x 0.53 mm GS-GasPro column (J&W Scientific). After approximately 7 min the valve was switched so that the effluent from the first column eluted onto a second 15 m x 0.32 mm polymethylsiloxane column connected to the mass spectrometer. The column switch was timed so that the C2 and C3 compounds eluted on the FID and all C4 and higher compounds eluted on the mass spectrometer. The GC program was as follows: 30 °C held for 2 min, then 8 °C/min up to 260 °C.

Calibration of the system was conducted with a mixture that contained the most commonly found hydrocarbons (75 compounds from ethane to n-undecane, purchased from Air Environmental), MTBE, and halocarbons (23 compounds from F12 to the dichlorobenzenes, purchased from Scott Specialty Gases). The standards were prepared in 6 L Silco-Steel canisters (Restek, Bellefonte, PA) by mixing three different standards through a multi-valve manifold using a Baratron absolute capacitance manometer (MKS Instruments, Andover, MA) to determine the pressure each standard added to the mixture. Prior to mixing approximately 0.2 ml of ultra pure water was added to the canister to humidify the mixture (for mixture stability). The concentrations in the mixture were in the range of 0.2 to 10 ppbv. Three point external calibrations were run prior to analysis, and one calibration check was run every 24 hours. If the response of individual compounds were more then 10% off, the system was recalibrated.

PAHs and nitro-PAHs
Upon receiving the samples from the field, the PUF plugs and XAD resins were Soxhlet extracted with acetone and the filters were microwave extracted with DCM (twice). The extracts were then concentrated by rotary evaporation at 20 °C under gentle vacuum to ~1 ml and filtered through 0.45 mm Acrodiscs (Gelman Scientific), rinsing the sample flask twice with 1 ml DCM each time. Approximately 100ul of acetonitrile was added to the sample and DCM was evaporated under a gentle stream of nitrogen.

For nitro-PAH, the extracts had to be pre-cleaned prior to GC/MS analysis using a solid phase extraction (SPE) technique. Clean up was conducted on a 3 ml aminopropyl Supelco SPE cartridge (LC-NH2), followed by semi-preparative HPLC. The HPLC (Waters equipped with Waters 484 variable wavelength UV detector) was operating under the following conditions: solvent A: hexane; solvent B: dichloromethane (DCM); flow rate: 3 ml/min; column: a semi-preparative scale 9.6 mm x 25 cm Chromegabonol Aminocyan column; detector: 254 nm. A fraction containing the n-PAH compounds was collected from the 25 to 35 minute elution intervals. The fractions were concentrated by rotary evaporation, and then taken just to dryness under a stream of nitrogen. The n-PAH fractions were dissolved in 100 ml of acetonitrile prior to analysis by GC/MS. Further details on the methodology for determining n-PAHs has been provided in the literature.
The samples were analyzed by the EI (electron impact) GC/MS technique, for PAH and n-PAH. A Varian Star 3800CX GC equipped with an 8200CX Automatic Sampler and interfaced to a Varian Saturn 2000 Ion Trap were used for these analyses. For PAH, injections (1 µL) were made in the splitless mode onto a 30 m 5% phenylmethylsilicone fused silica capillary column (CP Sil 8 CB, Varian) and for n-PAH on-column injection and 30 m 50% phenylmethylsilicone capillary column (RTX-50, Restek) were used.

Quantification of the individual compounds was obtained by a selective ion storage (SIS) technique, monitoring the molecular ion (or the characteristic ion) of each compound of interest and the corresponding deuterated internal standard, added prior to extraction. Calibration curves for GC/MS quantification were made for the most abundant and characteristic ion peaks of the PAH and n-PAH compounds using the deuterated species most closely matched in volatility and retention characteristics as internal standards.

APPENDIX B: Data Reduction

**Particulate Matter**
The basic form of the equation for the integrated TPM, PM\textsubscript{2.5} and PM\textsubscript{10} mass is:

\[
P_{\text{mass}} = (V_{\text{mix}} + V_{\text{sf}}) \times \left[ \frac{P_f}{V_{\text{sf}}} \right]
\]  

(1)

Where \(V_{\text{mix}}, V_{\text{sf}}\) are the volumes of the mixed air and sample flow, respectively. The resulting distance-specific mass emissions (g/mile) were obtained by dividing the integrated mass by the total distance traveled for that test:

\[
PM = \frac{P_{\text{mass}}}{\text{Distance}}
\]  

(2)

The “Tunnel Background” data is an average of the pre- and post- background data along with the actual test tunnel flow and distance traveled. For a given test run, the background equivalent mass is given as:

\[
P_{\text{mass bkgd}} = (V_{\text{mix, test}} + V_{\text{sf, test}}) \times \left[ \frac{P_{\text{f,bkgd}}}{V_{\text{sf,bkgd}}} \right]
\]  

(3)

Where \(V_{\text{mix, test}}, V_{\text{sf, test}}\) are the flow rates during the test, and the ratio \(P_{\text{f,bkgd}}\) to \(V_{\text{sf,bkgd}}\) is the averaged background particulate and sample flow, respectively, during the background tests.

**Volatile Organic Compounds**
The VOC data for each individual compound were treated similar to the PM\textsubscript{2.5} and PM\textsubscript{10} analyses, and then summed up into the respective group for reporting of results. The data are provided as “Ambient Background,” “Tunnel Background,” and “Test, Uncorrected”, as discussed before. The basic form of the equation for the integrated VOC mass is:

\[
VOC_{\text{mass}} = (V_{\text{mix}} + V_{\text{sf}}) \times [VOC_{\text{bag}}]
\]  

(4)

Where VOC\textsubscript{bag} is the concentration of the individual VOC compound in mass per unit volume units. The resulting distance-specific mass emissions (g/mile) are obtained by simply dividing the integrated mass by the total distance traveled for that test, as shown for PM above.